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(54) Title: METHOD FOR THE SELECTIVE REMOVAL OF METALS FROM CONCENTRATED METAL-CONTAINING STREAMS

(57) Abstract: The invention relates to a method for precipitating metals in the form of the metal sulphide from a concentrated solution with the aid of sulphide in a precipitator, wherein (a) the sulphide is added to the solution in the precipitator from a dilute stream of H<sub>2</sub>S gas that contains at most 25 % (V/V) H<sub>2</sub>S, or the sulphide is produced in the precipitator by biological reduction of sulphate, (b) seed material for the metal sulphide to be precipitated is added in a concentration of at least 5 g/l and (c) the precipitator is mixed well. During this operation, the metal sulphide precipitates in crystalline form.

**Method for the selective removal of metals from  
concentrated metal-containing streams**

**FIELD OF THE INVENTION**

5 The invention relates to a method by means of which, making use of sulphide, better separation can be achieved between metals which are close to one another in respect of their solubility in the form of the metal sulphide in the specific solution. The extent to which the metal sulphide precipitates formed using the new method can be dehydrated is also somewhat better than has been achieved hitherto.

10

**BACKGROUND**

Many processes are known by which metals are selectively recovered from concentrated streams in which several metals are present. Sulphide is frequently used for the selective separation of metals, separation being achieved on the basis of the differences in solubility of  
15 the various metal sulphides at different pHs.

The separation of copper and arsenic from spent electrolyte from electrorefining processes, such as are used on a large scale to produce pure copper, with the aid of sulphide has in particular been found to be extremely difficult up to now and is therefore also not often used.  
20 Usually the discharge stream is processed in a separate circuit consisting of the following process steps:

1. removal of copper by means of electrorecovery;
2. removal of arsenic by means of electrorecovery;
3. nickel sulphate crystallisation.

25

The electrolysis for the removal of copper and the removal of arsenic are closely linked to one another: at the point in time when the residual copper concentration becomes low (say a few grams per litre), arsenic starts to deposit together with the copper in the form of a copper/arsenic alloy. After forming at the cathode, the bulk of this alloy falls to the bottom of  
30 the cell. This means that the cells have to be cleaned regularly.

Apart from being labour-intensive, electrolytic removal of arsenic is hazardous to life because of the possible formation of lethal  $\text{AsH}_3$  gas if the copper concentration becomes too low ( $< 0.1 - 0.5 \text{ g/l}$ ). Moreover, the  $\text{Cu}_x\text{As}$  residue from the cells has to be further processed.

There are various processes for this.

Nickel sulphate is then crystallised out of the copper- and arsenic-free solution, which is by then highly acid, in evaporators or by supercooling. The crude nickel sulphate product is sold as such or is worked up further, for example for electroplating applications. Condensate and  
5 mother liquor are typically recycled for the water balance and, respectively, acid balance of the copper works.

Of course, numerous variants of the conventional process exist. For instance, there are various copper refineries in the world where arsenic is separated from copper and nickel by  
10 means of liquid/liquid extraction. Other refineries use ion exchange to keep the arsenic, antimony and bismuth concentrations at the required levels. Falconbridge in Ontario, Canada, uses an ion exchange system precisely for the selective removal of sulphuric acid from the discharge stream. Yet other works remove some of the copper in solution by crystallisation of copper sulphate. Finally, there are just a few copper works in the world  
15 where copper and arsenic are precipitated selectively from the discharge with the aid of sulphide. In Utah (US), the Kennecott Company uses 100 % H<sub>2</sub>S gas to achieve separation between copper and arsenic. Selectivities of only 70 % are achieved.

Apart from the separation of copper and arsenic from spent electrolyte, there are also other  
20 specific applications where the method according to the invention can have major advantages as far as selectivity and the capacity for dehydration are concerned, such as the separation of nickel from (bio)leach streams containing nickel, cobalt and iron and the recovery of zinc from magnesium bleed streams from zinc electrolysis processes. This novel method can also be used for the production of crystalline lead sulphide and copper sulphide.

25 Precipitation processes for the separation of metals are known from the literature. US 4 404 071 describes the precipitation of copper sulphide with the use of hydrogen sulphide. Monitoring of the redox potential is used to control the H<sub>2</sub>S feed in the continuous process. Selectivities of 70 % between copper and arsenic are obtained.

30 According to US 4,432,880 it is possible by means of sulphide precipitation to obtain lower metal concentrations in water contaminated with metals than can be obtained by the use of hydroxide precipitation alone. US 5,498,398 proposes the possibility of separating copper from arsenic, all of the metal being precipitated from the water in a first step. As, Sb and Bi

are then oxidised with oxygen and redissolved in the water. The residual precipitate is essentially copper sulphide. Arsenic, antimony and bismuth are then also reprecipitated with hydrogen sulphide. US 4,522,723 discloses biological reduction of sulphate in waste water containing heavy metals and precipitation of the heavy metals using the hydrogen sulphide resulting from the biological reduction. The precipitation of metal sulphide by the use of sulphur and sulphur dioxide is described in US 5,616,168. Separation of metals is achieved by controlled addition of sulphur and sulphur dioxide to the solution.

#### DESCRIPTION OF THE INVENTION

One problem with selective precipitation of metals by means of sulphide is that, as a result of local supersaturation, other metals also precipitate in addition to the desired metal, which other metals no longer easily go into solution. This problem can be partially solved by increasing mixing in the precipitation step. However, especially in the case of metals that are difficult to separate on the basis of their solubility, the mixing that can be achieved by means of, for example, a stirrer is often not really sufficient to achieve really high selectivities (> 95 %). The solution to this problem is, in combination with a high concentration of seed material in the precipitation step, to feed the sulphide to the liquid in a controlled manner, slowly and uniformly distributed. This can be achieved by feeding the  $H_2S$  into the precipitation step in the form of a gas, the  $H_2S$  concentration in the gas being kept low in a controlled manner and matched to the rate of precipitation in the liquid. By this means local supersaturation can be minimised to a substantial extent, as a result of which high selectivities are achievable. The extent to which the crystalline sulphide precipitates thus formed can be dehydrated is also substantially improved.

The  $H_2S$  required is added to a gas stream that is recirculated via the precipitation step, the  $H_2S$  concentration in the gas preferably being kept between 0.5 and 25 %. More preferentially, the concentration is kept between 1 and 15 % (V/V) and most preferentially between 2 and 10 %. The carrier gas used can be, for example, nitrogen gas. Preferably, the  $H_2S$  is produced in a bioreactor where sulphate, sulphur or another oxidised sulphur compound is reduced to  $H_2S$ . For bacteria and reaction conditions in such a process see, for example, WO 97/29055. In this case the  $H_2S$  is stripped from the bioreactor using the same gas as is used as carrier for the precipitation. The carrier gas used can thus also be hydrogen gas, that is used as an electron donor for sulphur/sulphate reduction, or methane and carbon dioxide produced in the bioreactor.

The process diagram for the sulphide precipitation can be seen in Figure 1. The water (1) [for example electrolyte] contaminated with metal ions is mixed in a mixer (MT1) with recirculated seed material. This material is then treated in the precipitator (Prec. 1) with controlled, dilute  $H_2S$  gas (7). The metal (for example copper) precipitates selectively in the precipitator. The effluent (3) is partially dehydrated in a thickener (Thick. 1). Part of the discharge from the bottom of the thickener (4) is returned to the mixer (MT1) as seed material. The remaining material is further dehydrated in a solid/liquid separator (S/L1). The solid (5) obtained has a low moisture content of approximately 40 % (m/m) and contains a specific metal sulphide (for example copper sulphide) of high purity. The wash liquid (6) from (S/L1) is returned to the thickener (Thick. 1). A subsequent metal can be selectively removed from the overflow (8) from the thickener (Thick. 1) by means of a second precipitation step. If necessary, the pH is controlled in the precipitation steps.

#### *Process control*

In order to be able selectively to precipitate the metal sulphide, the absolute  $H_2S$  feed must be matched to the metal burden fed to the precipitator. This is controlled by controlling the absolute  $H_2S$  feed on the basis of the redox potential in the liquid.

A second possibility for minimising the local supersaturation in a precipitation step, such that high selectivities and crystalline precipitates that can be dehydrated well are obtained, is to produce the  $H_2S$  in a controlled manner, slowly and uniformly, in the liquid. In this case it is possible, for example, to combine the bioreactor with the precipitation unit. A concentrated, metal-containing stream can be fed to a very well mixed bioreactor, the metal precipitating in the bioreactor, in which the metal sulphide concentration is kept high by employing solids retention, as crystalline metal sulphide as a consequence of the production of sulphide in the bioreactor. This is shown in Figure 2. This possibility is especially useful for separating off contaminating metals such as magnesium which do not precipitate or precipitate poorly as sulphide, such a metal being removed as a side stream from the production unit and the entrained metal produced, such as zinc, being precipitated and recycled to the production unit.

The water (1) containing metal (sulphate) is fed to a well-mixed bioreactor, preferably a gas lift loop reactor (R1), in which mixing is effected by recycling gas. It is optionally possible to feed in a gaseous electron donor for the biological reduction step, in the form of  $H_2$  (7), or a

small amount of inert gas, such as  $N_2$  (7), which can be used to remove the biologically produced  $CO_2$  via the gas bleed (8). Furthermore, seed material (4) is recirculated from the thickener. The effluent (2) from the reactor is dehydrated with the aid of a thickener (Thick. 3). The overflow (3) contains water from which sulphate and metals have been removed. Some of the discharge (4) from the bottom is recirculated. The remaining discharge from the bottom is further dehydrated with the aid of a solid/liquid separator (S/L3). The product (5) is metal sulphide containing approximately 40 % moisture. The wash water (6) from the solid/liquid separator (S/L3) is returned to the thickener (Thick. 3). The bioreactor can also be constructed with an internal settler. In this case a smaller stream is returned to the thickener from the bioreactor.

#### *Process control*

In this case also  $H_2S$  production can be controlled on the basis of the redox signal in the liquid in the bioreactor. Another possibility is on-line sulphide determination in the liquid or gas phase.

#### EXAMPLES

##### **Example 1:**

A 1 l stirred tank reactor containing a synthetic electrolyte solution was fed, through a glass pipe, with a gas mixture containing  $H_2S$  (25 % (V/V)). The effluent gas was passed through a wash bottle containing sodium hydroxide solution to absorb excess  $H_2S$ . No excess  $H_2S$  was determined during the precipitation. The reaction temperature was 60°C and the pressure was 1 bar. The electrolyte solution contained 10.47 g/l copper, 6.75 g/l arsenic, 200 g/l sulphuric acid and 60 g/l copper sulphide as seed material. It can be seen from Table 1 that copper and arsenic precipitated simultaneously. The selectivity for copper was only 50 to 60 %. The effluent filtration rate was 313 kg solids per  $m^2$  per hour. X-ray diffraction showed that the copper sulphide was crystalline.

In an analogous manner a 1 l stirred tank reactor containing a synthetic electrolyte solution was fed, through a glass pipe, with a gas mixture containing  $H_2S$  (15 % (V/V)). The effluent gas was passed through a wash bottle containing sodium hydroxide solution to absorb excess  $H_2S$ . No excess  $H_2S$  was determined during the precipitation. The reaction temperature was 60°C and the pressure was 1 bar. The electrolyte solution contained 10.34 g/l copper, 6.85 g/l arsenic, 200 g/l sulphuric acid and 60 g/l copper sulphide as seed material. It can be seen

from Table 2 that more copper precipitated than arsenic. The selectivity for copper was about 60 - 70 %. The effluent filtration rate was 142.5 kg solids per m<sup>2</sup> per hour. X-ray diffraction showed that the copper sulphide was crystalline.

5 Table 1: Change in the metal concentration with time

Time [min]	Cu recovery % [(m/m)]	As recovery [% (m/m)]	Selectivity [%]
0	0.00	0.00	
15	4.59	2.71	62.91
30	13.94	6.09	69.58
45	16.90	17.03	49.80
60	28.66	25.91	52.53
90	48.36	40.24	54.58
120	67.41	55.14	55.01
180	97.45	88.20	52.49
240	100.00	87.95	53.21

Table 2: Change in the metal concentration with time

Time [min]	Cu recovery % [(m/m)]	As recovery [% (m/m)]	Selectivity [%]
	0.00	0.00	
0	2.32	0.00	100.00
15	6.11	3.39	64.33
30	14.09	7.23	66.08
45	22.72	10.68	68.02
60	34.78	15.09	69.74
90	46.26	24.65	65.24
120	70.99	36.35	66.14
180	86.06	42.88	66.75
210	92.28	56.70	61.94
240	99.70	70.26	58.66

10 In an analogous manner a 1 l stirred tank reactor containing a synthetic electrolyte solution

was fed, through a glass pipe, with a gas mixture containing H<sub>2</sub>S (5 % (V/V)). The effluent gas was passed through a wash bottle containing sodium hydroxide solution to absorb excess H<sub>2</sub>S. No excess H<sub>2</sub>S was determined during the precipitation. The reaction temperature was 60°C and the pressure was 1 bar. The electrolyte solution contained 9.78 g/l copper, 6.09 g/l arsenic, 200 g/l sulphuric acid and 60 g/l copper sulphide as seed material. It can be seen from Table 3 that only copper precipitated. A very high selectivity for copper was achieved (> 95 %). The effluent filtration rate was 173.15 kg solids per m<sup>2</sup> per hour. X-ray diffraction showed that the copper sulphide was crystalline.

Table 3: Change in the metal concentration with time

Time [min]	Cu recovery % [(m/m)]	As recovery [% (m/m)]	Selectivity [%]
0	0.00	0.00	
60	5.26	0.00	100.00
120	10.75	0.00	100.00
180	22.24	0.00	100.00
240	28.71	2.20	92.89
300	37.70	0.61	98.41
360	52.97	0.00	100.00

The results of the three tests are shown once again in Figure 3. It can be seen that the selectivity for copper precipitation increases substantially with lower H<sub>2</sub>S concentrations in the gas.

#### Example 2:

Treatment of magnesium bleed from the zinc electrolysis process

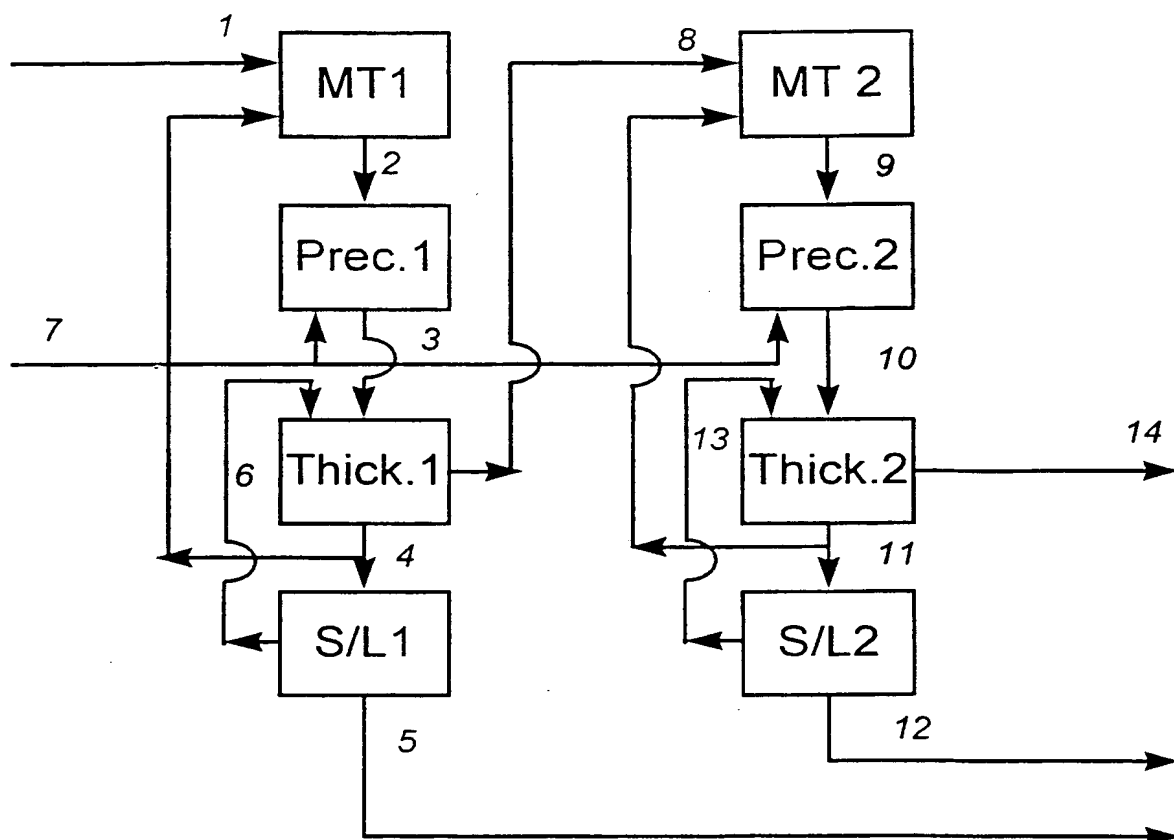
25 litres per hour magnesium bleed containing 150 g/l zinc, 16 g/l magnesium and 280 g/l sulphate was fed directly to a sulphate-reducing bioreactor. The bioreactor consisted of a 5 m<sup>3</sup> gas lift loop reactor with a hydrogen gas recycle for mixing and transfer of hydrogen gas to the bacteria for the sulphate reduction process. Up to 150 g/l ZnS was accumulated in the bioreactor and the effluent from the bioreactor contained 50 mg/l sulphide, < 0.1 mg/l zinc and < 100 mg/l sulphate. The ZnS produced was crystalline and could be dehydrated easily to produce a paste containing 20 to 40 % moisture.



**CLAIMS**

1. Method for precipitating metals in the form of the metal sulphide from a concentrated solution with the aid of sulphide in a precipitator, characterised in that (a) the sulphide is added to the solution in the precipitator from a dilute stream of H<sub>2</sub>S gas that contains at most 25 % (V/V) H<sub>2</sub>S, or the sulphide is produced in the precipitator by biological reduction of sulphate, (b) seed material for the metal sulphide to be precipitated is added in a concentration of at least 5 g/l and (c) the precipitator is mixed well.
2. Method according to Claim 1, characterised in that (b) seed material for the metal sulphide to be precipitated is added in a concentration of at least 10 g/l
3. Method according to Claim 2, characterised in that (a) the sulphide is added from a dilute stream of H<sub>2</sub>S gas that contains 1 - 15 % H<sub>2</sub>S
4. Method according to one of Claims 1-3, characterised in that (a) the sulphide is added such that the concentration of dissolved sulphide remains below 10 mg/l.
5. Method according to one of Claims 1-4, characterised in that the metal solution originates from an electrorecovery process.
6. Method according to Claim 5, characterised in that copper sulphide is selectively precipitated.
7. Method according to Claim 1 or 2, characterised in that (a) the sulphide is produced by biological reduction of sulphate and the metal solution is added with a metal concentration of at least 2 g/l, preferably more than 5 g/l and in particular more than 10 g/l.
8. Method according to one of Claims 1-7, characterised in that the pH is adjusted such that the metal sulphide to be precipitated precipitates but a metal sulphide that has a higher solubility at the same pH does not precipitate.
9. Method according to one of Claims 1-8, characterised in that the metal sulphide is precipitated in crystalline form.

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**Fig 1**

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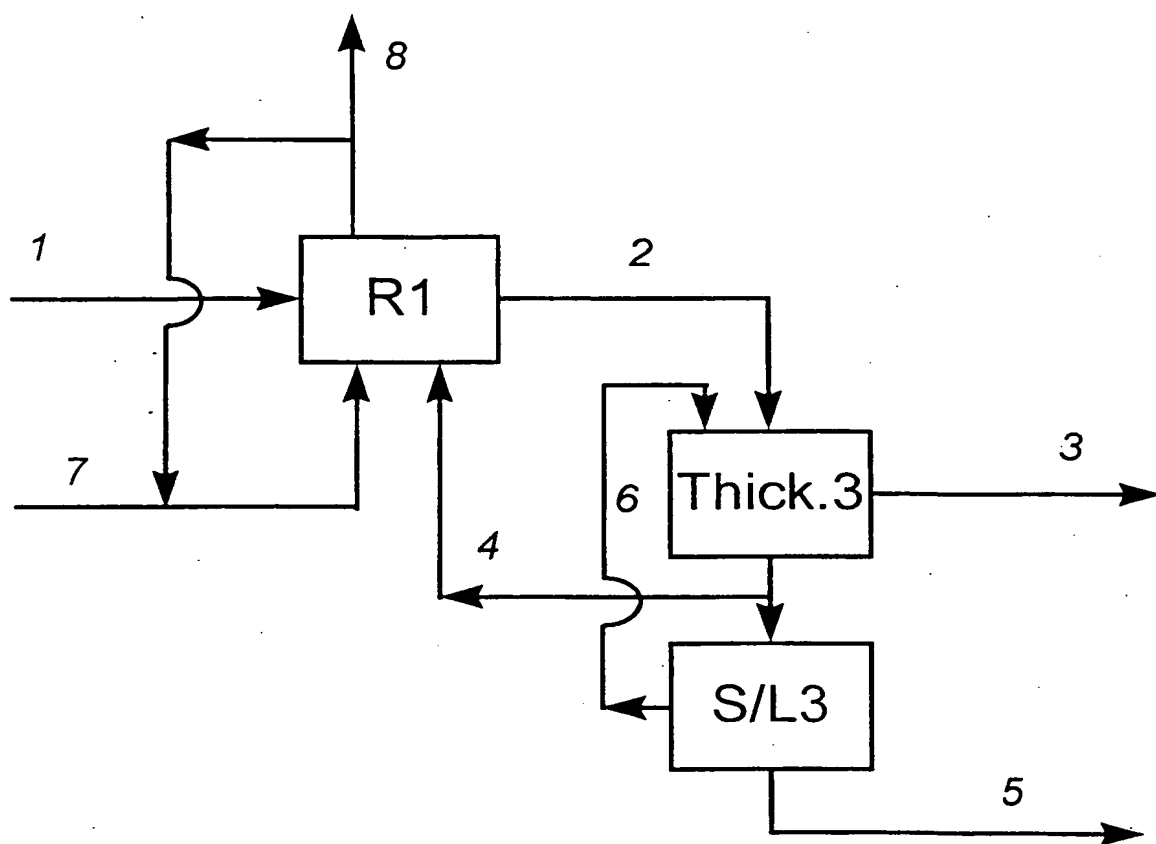
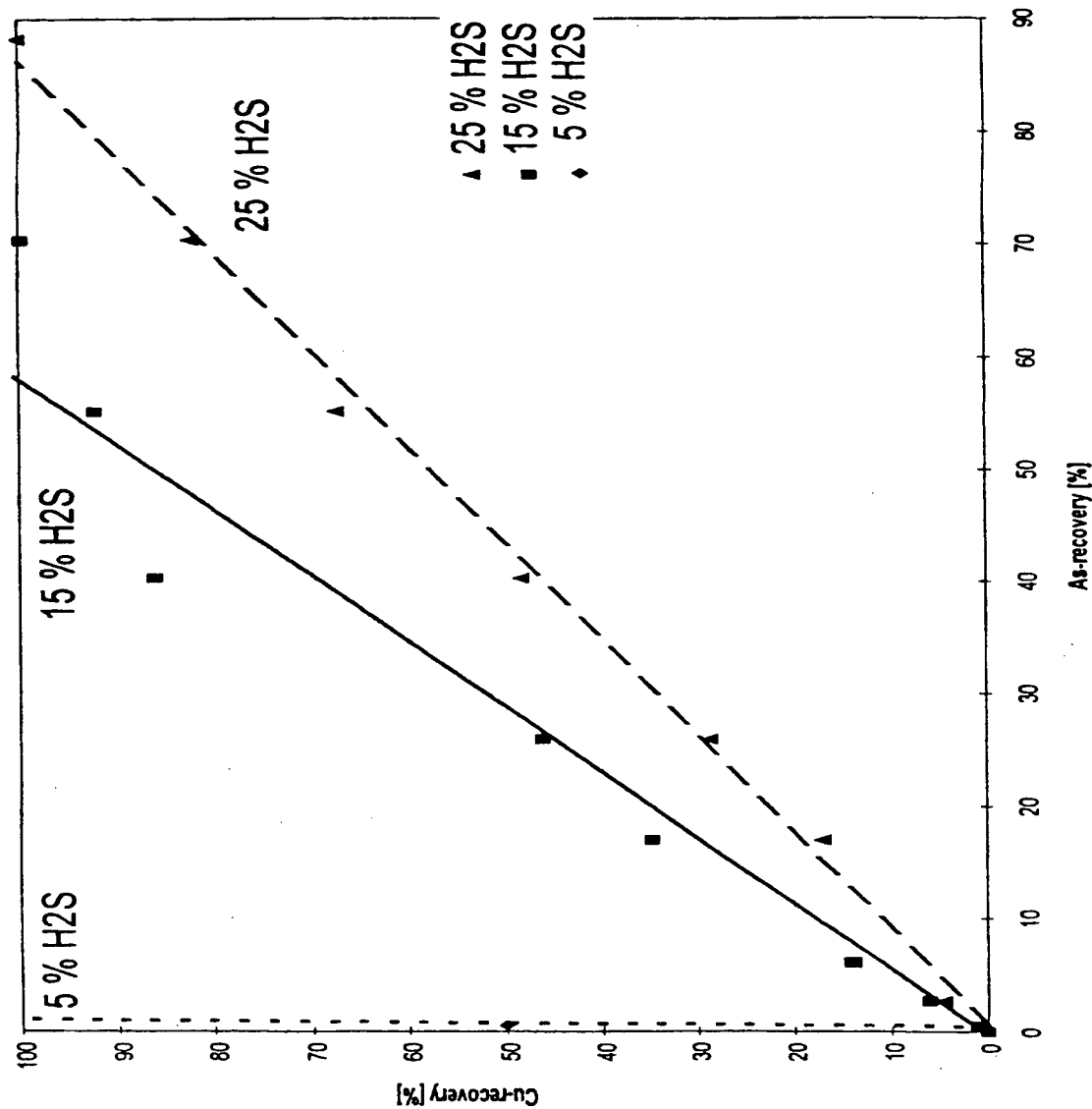
**Fig 2**

Fig 3



# INTERNATIONAL SEARCH REPORT

Internatic Application No

PCT/NL 00/00841

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01G1/12 C01G3/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 522 723 A (KAUFFMAN JIM W ET AL) 11 June 1985 (1985-06-11) cited in the application	1
X	the whole document	7-9
A	US 1 468 988 A (CHARLES BERTHELOT) 25 September 1923 (1923-09-25) the whole document	1,3,6
Y	DE 14 67 316 A (DEUTSCHE AKADEMIE DER WISSENSCHAFTEN ZU BERLIN) 9 January 1969 (1969-01-09) the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4522723	A	11-06-1985	NONE	
US 1468988	A	25-09-1923	NONE	
DE 1467316	A	09-01-1969	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)